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BUREAU OF CHEMISTRY—BULLETIN No. 89.

H. W. WILEY, Chief of Bureau.

INJURY TO VEGETATION BY SMELTER FUMES.

BY

J. K. HAYWOOD,

Chief, Insecticide and Agricultural Water Laboratory.



WASHINGTON:

GOVERNMENT PRINTING OFFICE.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY,

Washington, D. C., November 15, 1904.

SIR: I have the honor to transmit for publication the results of an investigation made by the Chief of the Insecticide and Agricultural Water Laboratory of this Bureau, at the request of the Department of Justice, in regard to the extent of the injury inflicted on surrounding vegetation by a copper-smelting plant located near Redding, Cal. I recommend that this report be published as Bulletin No. 89 of the Bureau of Chemistry, the consent of the Department of Justice to such publication having been obtained.

Respectfully,

H. W. WILEY, *Chief.*

Hon. JAMES WILSON,
Secretary of Agriculture.



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INJURY TO VEGETATION BY SMELTER FUMES.

INTRODUCTION.

The investigation described in this bulletin was undertaken at the request of the United States Department of Justice in consequence of a suit brought by the United States against the Mountain Copper Company (Limited), a corporation operating a large copper-smelting plant situated near Redding, Shasta County, Cal. The investigation was made to show whether or not the fumes from this plant are injurious to vegetation, and, if such injury exists, over how large an area it extends. While the company is willing to acknowledge damage over a certain limited area surrounding the plant, it was thought by the plaintiff in the case that this damage extended over a much larger area than was acknowledged by the defendant.

The writer was detailed to inspect the disputed area and take such samples for chemical analysis as might appear to be necessary. It was constantly borne in mind during this investigation that for a certain distance injury to vegetation was acknowledged, so that the taking of samples in this area was unnecessary. Consequently all samples of vegetation were taken either on the extreme edge or outside of the area of acknowledged damage, which, when plotted on the map, shows itself in the form of an irregular ellipse surrounding the smelter and extending about 3 miles north, $2\frac{1}{2}$ miles south, 1 mile east, and 3 miles west. About 60 samples of the trees, water, soil, and ore were taken and subjected to chemical analysis, from which very definite results have been obtained. It might be well to describe first the situation of the smelter and the general appearance of the vegetation in the region as it presented itself to the chemist.

LOCATION OF SMELTER AND APPEARANCE OF SURROUNDING VEGETATION.

The smelter is situated in a narrow valley, or what might almost be termed a cut between the mountains. Its highest chimneys are far below the level of the surrounding land. In a northerly and westerly direction other narrow gulches branch off from this main one, so that the fumes have a tendency to keep together and drift for long distances in these natural chimneys. In a southerly direction the fumes,

after drifting over one high hill, have an uninterrupted sweep down the valley of the Sacramento. In an easterly direction the fumes pass, in the main, down the valley of a small stream and finally find outlet at the river, where they have a nearly uninterrupted sweep in both a southerly and an easterly direction.

Immediately surrounding the smelting works practically all vegetation was entirely dead. Nothing was left of the trees but the barkless trunks, and no green grass was to be seen. In a northerly direction, as far as Copley (about $3\frac{1}{2}$ miles), it was noted that large numbers of trees were either dead or dying, this being especially true of pines. Even for a mile and more beyond Copley numbers of the trees were dead, and others though living did not appear to be strong and healthy. In an easterly direction and beyond the river the damage was not so great, yet even here for $2\frac{1}{2}$ to 3 miles and more the leaves of nearly all oak trees were turning brown and dying.

In a southerly direction great damage was observed to all classes of trees for about 3 miles, or to the southern road running between Redding and Shasta. Still farther south, in Happy Valley (about 9 or 10 miles distant from the smelter), it was observed that large numbers of fruit trees, especially the peaches, which are very sensitive to injurious substances, were badly injured. This injury showed itself in the following way: The leaves would turn prematurely red and yellow (just as they do when sprayed with Paris green containing too much soluble arsenic) and drop off of the branches, leaving the fruit exposed, sometimes for 2 to 3 feet from the end of the branch. The trees did not appear to be suffering from a lack of water, nor from disease or insect pests, so that this injury was very likely due to the sulphur dioxid fumes. Further than this, several ranchers were interviewed, who said that when the wind was in a southerly direction the odor of the fumes could be plainly detected in their orchards and that soon after this the leaves usually began to drop. In a westerly direction great damage to a large number of trees was observed all the way to Whisky Town, about 5 miles from the smelter. Beyond Whisky Town the injury was not so great, but for a mile and more some of the trees were dead and large numbers did not appear to be vigorous and healthy, i. e., they were stunted in growth, had much less than the normal amount of foliage, and what foliage there was did not have a healthy green color.

Before describing the investigation as made, the principles of elementary chemistry involved will be given for the benefit of readers who, though not chemists, may desire to use the data.

CHEMICAL PRINCIPLES UNDERLYING THE INVESTIGATION.

The ore used by the Mountain Copper Company consists largely of sulphids of iron and copper. During the process of extracting the copper it is first calcined in appropriate furnaces to get rid of a large



VIEW OF THE SMELTER IN OPERATION.





COUNTRY ABOUT 1 MILE WEST OF SMELTER.



part of the sulphur. It is then fused with a siliceous flux, which removes more of the sulphur and a large part of the iron. This process is repeated until a product quite rich in copper is obtained. Finally, the impure copper is placed in a blast furnace with a siliceous lining, where the remainder of the impurities, consisting of iron, sulphur, etc., are either fluxed or burned off.

In practically all of these processes the sulphur originally present in the ore is burned and given off into the air, principally as sulphur dioxide, but to some extent as sulphur trioxide. For each pound of sulphur burned 2 pounds of sulphur dioxide are formed and given off into the atmosphere, a part of which acts directly on the foliage of the trees. Sooner or later, however, all of the sulphur dioxide is changed by the action of the oxygen of the air into sulphur trioxide, and it is in this form that we may expect to find it in the foliage of trees. The moisture present in the air unites with this sulphur trioxide to form the highly corrosive compound sulphuric acid, which in its turn acts upon the delicate foliage.

One other point should be mentioned. The foliage of all plants naturally contains some sulphur trioxide that the tree has absorbed from the ground through its roots. The sulphur trioxide thus absorbed, however, is not in the free state, as it is when formed in the air by the burning of sulphur, but is combined with other substances which render it entirely harmless. The sulphur trioxide absorbed from the air is in a free and very corrosive state. It will thus be seen that all trees examined will contain sulphur trioxide, and that this sulphur trioxide may be derived either from the harmless form in the earth or from the harmful form in the air. If two trees grow near each other in the same soil and are about equally vigorous, the sulphur trioxide absorbed from the earth is apt to be about the same in both trees. While this may fail in individual cases, it will be true in the majority of cases. Now, if the percentage of sulphur trioxide both in the dry foliage and in the ash of the dry foliage of one tree of a certain species is much higher than it is in another of the same species standing close by, there is an indication that this may have come from the sulphur trioxide or dioxide of the air; if the percentage of sulphur trioxide both in the dry foliage and in the ash of the dry foliage of *many* trees of a certain species is higher than it is in near-by trees of a like species, it is almost absolute proof that it must have come from the sulphur trioxide or dioxide of the air. Going one step further, if the trees containing the larger amounts of sulphur trioxide have been injured, while those containing the smaller amounts of sulphur trioxide have not been injured, it is more than probable that the former trees have been injured by fumes containing sulphur dioxide or trioxide. The results of the investigation, to determine this point, are given in the following pages.

EXPERIMENTAL WORK.

VISIBLE INJURY TO VEGETATION BY SULPHUR DIOXID.

COMPILED DATA.

First, it must be ascertained whether sulphur dioxide does injure vegetation, how small a quantity may be injurious, and through what organs of the plant such injury takes place. Light is thrown on these points by the work of several foreign chemists. M. Freytag^a showed conclusively by experimental work that the sulphur dioxide and trioxide in the air does not injure the plant through the medium of the roots. For this purpose he watered vigorous wheat, oat, and pea plants night and morning with 20 liters of water, containing in one case 4 grams of sulphurous acid and in the other case 5 grams of sulphuric acid. This continued for forty-five days. At the end of this time the amounts of acid were raised to 6 grams of sulphurous and 7.5 grams of sulphuric acid for fifteen days. Then for fifteen days the amounts of acid were increased to 8 grams of sulphurous and 10 grams of sulphuric. At the end of this time no injury to the plants could be noted, and the yield of crop was as great in the case of the plants treated with acid as in the case of untreated plants.

J. von Schroeder and W. Schmitz Dumont,^b by an investigation made in 1896, showed that the injury to vegetation by sulphur dioxide is not by means of the roots, but through the leaves, and that even extremely minute quantities of sulphur dioxide are injurious. They used pines, and conducted the experiment in the following manner:

(a) Part standing above the earth only treated with sulphur dioxide.

(b) Part standing above the earth and earth in which plant was grown treated with same strength of sulphur dioxide.

(c) The same amount of sulphur dioxide, in water solution, as used in (a) and (b) added to the earth around the roots.

(d) Control plant not treated.

On the first day a concentrate of 1:20,000 parts of sulphur dioxide was used, on the second 1:10,000, on the third, fourth, and fifth, 1:5,000. Without going into the details of the experiment, it will suffice to say that this treatment seriously injured (a); injured (b), but not to so great an extent as (a), and did not injure (c) in any way. The control plant was in good condition at the end of the experiment.

Further work showed that upon fumigating pines for 109 times with 1 part of sulphur dioxide to 100,000 parts of air great injury was inflicted. A large number of the needles turned brown or yellow, and practically all became partly yellow. Upon fumigating 9 pines for 583 times with 1 part of sulphur dioxide to 1,000,000 parts of air injury was also noted. Other chemists and biologists have worked upon this same subject, among them being A. Stockhardt,^c A. Wieler,^d

^a Mitt. d. königl. landw. Akad., Poppelsdorf, 1869, 2.

^b Tharander forstl. Jahrb., 1896, 46: 1.

^c Tharander forstl. Jahrb., 1871, 21: 230. ^d Ber. d. botan. Ges., 1902, 20: 536.

etc., but enough data have been given to show the present status of the case.

EXPERIMENTS MADE IN THE BUREAU OF CHEMISTRY.

In order that the author might be able to testify from his own experience that minimum amounts of sulphur dioxide are injurious to vegetation, the following experiments were made:

A cabinet 2 by 2 feet at the base and 4 feet high was built, having glass sides like a greenhouse, and so arranged that the whole top of the cabinet could be lifted from the wooden base to allow the introduction of rather large plants. (See fig. 1.) At the front a small door about 1 foot square was placed to allow the operator to arrange the plants in the cabinet and introduce the vessel containing the fluid from which the sulphur dioxide was to be made. The connections between the top of the cabinet and the base and between the door and framework of the side of the cabinet were made with rubber strips and screw clamps, and thus the surfaces could be drawn close together and the connections made as nearly air-tight as possible, so that practically none of the sulphur dioxide could escape.

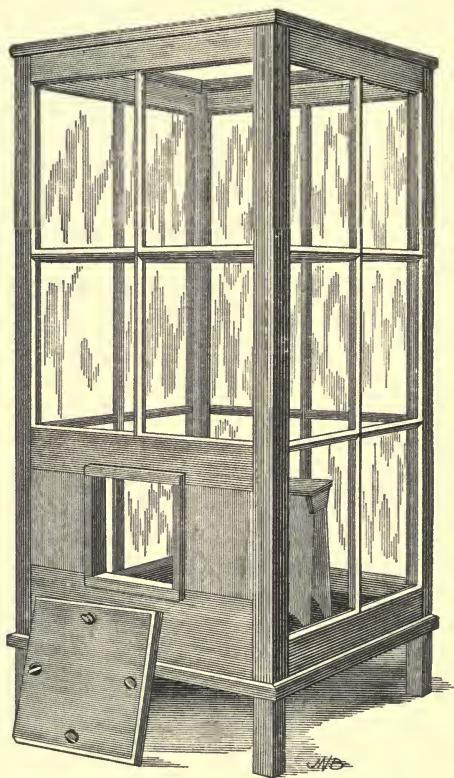


FIG. 1.—Cabinet in which plants were fumigated.

In preparation for an experiment the plant was first placed in the case and the top screwed tightly to the base. A known weight of carbon disulphid in alcoholic solution held in a platinum dish was then introduced into the chamber, such a weight of carbon disulphid being used that the sulphur dioxide formed by burning bore a definite ratio to the weight of air in the box. The alcoholic solution of carbon disulphid was then quickly lighted and the door on the front adjusted. A small electric fan previously placed in the chamber was then started from the outside to equalize the amount of sulphur dioxide in all parts of the fumigation chamber. After the burning was completed the fan was stopped. In no case did the amount of alcohol

and carbon disulphid used in burning give off enough heat to raise the temperature of the chamber above that of an ordinary greenhouse. After an hour of this treatment the door was opened and the air in the box pumped out by means of the fan. The process was then repeated, so that each plant received from three to four fumigations per day. At night the plants were removed from the fumigation chamber. Control plants were always placed alongside the fumigation chamber, and these were removed from the room during the time that the sulphur dioxid was being pumped out of the chamber. Potted Australian pines of about three years' growth and young cowpeas were used in the experiment. The following results were obtained:

(a) Pine tree. Fumigated with 1 part of sulphur dioxid to 100 parts of air (by weight). After 3 one-hour fumigations the needles began to droop badly and turned from a bright to a gray, green. After 6 one-hour fumigations practically all of the needles were drooping and nearly all had turned either yellow or brown. The pine was evidently badly injured, although the control plant was in good condition.

(b) Pine tree. Fumigated with 1 part of sulphur dioxid to 1,000 parts of air. After 3 one-hour fumigations the pine needles began to droop and some to turn yellow. After 9 one-hour fumigations all of the needles were drooping and had turned brown and yellow. Tree evidently badly injured, although control plant was in good condition.

(c) Pine tree. Fumigated with 1 part of sulphur dioxid to 10,000 parts of air. After 25 one-hour fumigations the pine needles began to droop, and some were slightly grayish and others brownish. After 50 one-hour fumigations a large number of the needles had turned brown, and the remainder looked extremely unhealthy. This same pine was now fumigated with 1 part of sulphur dioxid to 30,000 parts of air. After 18 such fumigations it was removed and found to have been greatly injured. About one-half of the needles were brown and dead and the remainder were sickly looking and yellow. The control plant was in good condition.

(d) Two cowpeas. Fumigated with 1 part of sulphur dioxid to 10,000 parts of air. After 3 one-hour fumigations about one-half the leaves of both had shriveled up and fallen. After 18 one-hour fumigations all of the leaves of both plants had shriveled up and fallen. The cowpeas were then subjected to three or four more fumigations of the same strength and taken out and watered to see if they would grow again, but they could not be revived. The control cowpeas in this experiment were in good condition.

(e) Pine tree. Fumigated with 1 part of sulphur dioxid to 30,000 parts of air. After 50 one-hour fumigations the needles were drooping, and most of them looked yellow and sickly.

This experiment was not continued further, it having been shown to the author's satisfaction that extremely minute quantities of sulphur dioxid were injurious to vegetation.

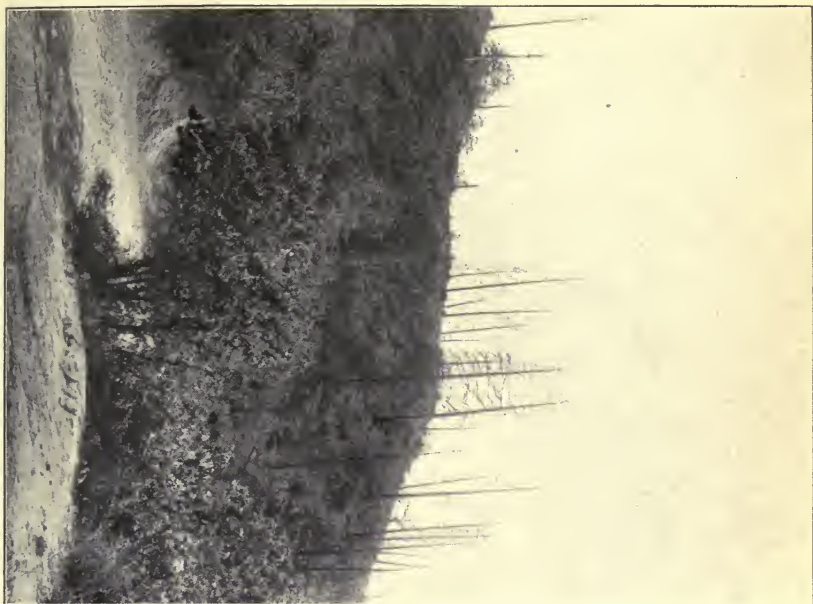


FIG. 1.—VIEW ABOUT 3 MILES WEST OF SMELTER.



FIG. 2.—VIEW ABOUT 3½ MILES WEST OF SMELTER.





FIG. 1.—ORCHARD ABOUT $2\frac{1}{2}$ MILES SOUTHWEST OF SMELTER.



FIG. 2.—COUNTRY ABOUT 2 MILES SOUTH OF SMELTER.



SULPHUR TRIOXID CONTENT OF THE FOLIAGE OF FUMIGATED AND
NONFUMIGATED PLANTS.

COMPILED DATA.

The next point to determine is whether treating these plants with sulphur dioxide increases the sulphur trioxid content of the leaves so that it is present in larger quantities in the treated plants than in the untreated ones. As a necessary consequence of such an increase the sulphur trioxid content of the ash of a fumigated plant would be apt to be higher than the sulphur trioxid content of the ash of an unfumigated plant. This can be determined by making analyses of fumigated and control plants.

In the work of von Schroeder and Schmitz Dumont, which has already been mentioned, a chemical analysis of the pine needles of the fumigated and control plants was made and the following results obtained:

TABLE 1.—*Comparison of analyses of pine needles from plants variously treated with sulphur dioxide and from a control plant (J. von Schroeder and W. Schmitz Dumont).*

Description.	Ash in dry needles.	Sulphur trioxid.		
		In dry needles.	In ash.	In earth.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
(a) Plant only treated with sulphur dioxide	5.72	0.581	10.16	0.0199
(b) Plant and earth treated with sulphur dioxide	5.47	.438	8.01	.0186
(c) Earth only treated with sulphur dioxide	5.67	.437	7.71	.0242
(d) Control plant	5.60	.407	7.27	.0184

It will be noted that the sulphur trioxid of the treated plants is in excess of that in the untreated plant, and that the percentage of sulphur trioxid in the ash of the treated plants is higher than the percentage of sulphur trioxid in the ash of the control plant. This increase in the case of (c), where only the earth was treated, is undoubtedly due to the increased amount of sulphur trioxid in the soil.

In the experiment before mentioned, in which pines were treated 583 times with 1 part of sulphur dioxide to 1,000,000 parts of air, the following results were obtained on subjecting the needles to a chemical examination.

TABLE 2.—*Analyses of injured and uninjured needles on fumigated pines, compared with those of the control plant (J. von Schroeder and W. Schmitz Dumont).*

Description.	Ash in dry needles.	Sulphur trioxid.	
		In dry needles.	In ash.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Needles fallen from pine No. 1	5.87	0.578	9.85
Injured needles from pine No. 4	5.54	.509	9.19
Injured needles from pines Nos. 2 and 3	4.72	.519	11.00
Mean for all injured needles	5.38	.535	9.94
Sound needles of control plant	4.91	.276	5.62

TABLE 2.—*Analyses of injured and uninjured needles, etc.*—Continued.

COMPARISON OF YOUNG AND OLD NEEDLES ON PINES NOS. 2 AND 3.

Description.	Ash in dry needles.	Sulphur trioxid.	
		In dry needles.	In ash.
(1) This year's needles: <i>a</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
(a) Injured.....	3.97	0.528	13.30
(b) Uninjured.....	4.52	.280	6.11
(2) Needles of previous years:			
(a) Injured.....	5.40	.512	9.48
(b) Uninjured.....	5.28	.272	5.15

a "This year's needles" refers to the young needles grown in the same year as that in which the experiment was made; "needles of previous years" are those which remain over from the growth of previous years.

ANALYSES MADE IN THE BUREAU OF CHEMISTRY.

A chemical examination of the needles from the pines and leaves from the cowpeas used in the author's experiments gave the following results:

TABLE 3.—*Effect on pine trees and cowpeas of fumigating with varying strengths of sulphur dioxid, as shown by the sulphur trioxid determined in the foliage.*

Serial No.	Description.	Ash in dry leaves.	Sulphur trioxid.	
			In dry leaves.	In ash.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1385	Pine tree used as control.....	2.50	0.237	9.20
1386	Pine tree treated with sulphur dioxid 1-100.....	2.86	.525	18.18
1385	Pine tree used as control.....	2.50	.237	9.20
1387	Pine tree treated with sulphur dioxid 1-1,000.....	2.96	.665	22.30
1357	Pine tree used as control.....	2.87	.247	8.36
1355	Pine tree treated with sulphur dioxid 1-10,000.....	2.17	.335	15.20
1351	Cowpea used as control.....	18.00	.477	2.61
1353	Cowpeas treated with sulphur dioxid 1-10,000.....	19.75	1.835	9.27

It will at once be seen from the three tables given above that all plants treated with sulphur dioxid contain more sulphur trioxid in their leaves than plants not so treated, and that the percentage of sulphur trioxid in the ash of fumigated trees is higher than it is in trees that have not been fumigated. Consequently, a method is at once suggested for determining whether the trees around the plant of the Mountain Copper Company have been killed by the fumes or have died from some other cause.

SULPHUR TRIOXID CONTENT OF THE FOLIAGE OF TREES SURROUNDING SMELTERS.

ANALYSES OF FOLIAGE ABOUT THE COPPER SMELTER NEAR REDDING, CAL.

Having now shown that trees are killed by minute quantities of sulphur dioxid and that usually this injury is accompanied by an increased content of sulphur trioxid in the leaves and ash, the next step is to see whether the dead trees around the Mountain Copper Company's works usually contain more sulphur trioxid than those trees which stand close by, and therefore have the same soil, but have not been killed. The results of these determinations are contained in Table 4.

TABLE 4.—*Sulphur trioxid and ash in foliage of trees around smelter.*

[Calculated to dry basis.]

Serial No.	Description of sample.	Location.	Direction and approximate distance from smelter.	Ash in leaves or needles.	Sulphur trioxid.		Designation of groups.
					In leaves.	In ash.	
a 1236	Pine needles: Entirely dead tree.	On company's railroad.	3½ miles north-west.	Per ct.	Per ct.	Per ct.	A
a 1237	Uninjured			{ 5.71 4.37	0.84 .58	14.71 13.27	
a 1242	Entirely dead	East of Shasta	2½ miles south.	{ 5.03 3.95	1.59 .87	31.61 22.02	B
a 1241	Uninjured						
1243	Bean leaves:	Trinity County road, between Whisky Town and Shasta.	2½ miles south-west.	{ 25.03 18.87	1.06 .95	4.23 5.19	C
1245	Injured vine.						
1248	Uninjured vine.						
1248	Peach leaves:	do	do	{ 15.75 13.13	.72 .51	4.57 3.88	D
1247	Injured tree.						
1249	Uninjured tree.	do	3½ miles south-west.	{ 5.01 5.35	.64 .74	12.77 13.83	E
1250	Dead tree.			{ 4.90 4.66	.87 .81	17.75 17.38	
1253	Uninjured tree.	200 yards north of Whisky Town.	5 miles west.	{ 4.90 4.66	.87 .81	17.75 17.38	F
1254	Uninjured tree.						
1255	Blackberry leaves:	At Whisky Town.	5 miles west	{ 5.52 6.38	.47 .27	8.52 4.08	G
1256	Nearly dead bush			{ 6.38 7.11	.27 .59	4.08 8.30	
1257	Uninjured bush	do	do	{ 7.11 6.38	.59 .27	8.30 4.08	H
1256	Uninjured bush						
1258	Pine needles:	do	do	{ 3.07 4.94	.55 .57	17.91 11.54	I
1260	Dead tree.			{ 4.94 2.53	.57 .56	11.54 22.13	
1259	Uninjured tree.	do	do	{ 2.53 4.94	.56 .57	22.13 11.54	J
1260	Uninjured tree.						
1261	Injured tree.	About 1 mile west of Whisky Town.	6 miles west.	{ 4.21 3.50	1.16 .68	27.55 19.43	K
1262	Uninjured tree.						
1263	Dead tree.	On the south road between Redding and Shasta.	8 miles south	{ 3.25 3.59	.51 .89	15.69 24.79	L
1264	Uninjured tree.						
1265	Oak leaves:	do	do	{ 8.88 9.18	.53 .25	5.96 2.72	M
1266	Injured tree.						
1267	Uninjured tree.	Halfway between Keswick and Copley.	2 miles north-east.	{ 5.30 5.17	.90 .74	16.95 14.31	N
a 1268	Dead tree.						
1270	Uninjured tree.	At Copley	3½ miles north-east.	{ 4.44 4.36	.71 .65	16.00 14.91	O
1271	Dead tree.			{ 4.36 5.71	.65 1.02	14.91 17.83	
1272	Uninjured tree.	do	do	{ 5.71 4.44	.65 .65	14.59 14.59	P
1274	Nearly dead tree			{ 4.44 5.79	.65 1.25	14.59 21.59	
1273	Uninjured tree.	do	do	{ 5.79 4.44	1.25 .65	21.59 14.59	Q
1274	Uninjured tree.						
1275	Oak leaves:	East of river	1½ miles east	{ 6.29 5.81	.32 .40	5.09 6.89	R
1276	Nearly dead						
1277	Uninjured	do	do	{ 3.27 2.84	.66 .57	20.19 20.07	S
1278	Pine needles:						
1280	Injured	do	2½ miles east	{ 7.88 7.23	.51 .41	7.47 5.67	T
1279	Uninjured			{ 7.23 5.90	.41 .60	5.67 10.17	
1281	Injured	do	do	{ 5.90 7.23	.60 .41	10.17 5.67	U
1279	Uninjured						
1283	Pine needles:	Happy Valley, on road.	9 miles south	{ 2.46 3.24	.89 .64	36.18 19.75	V
1284	Injured						
1285	Uninjured	Happy Valley, on Klummann ranch.	do	{ 10.75 8.29	.45 .32	4.19 3.86	W
1286	Injured			{ 8.29 12.10	.32 .36	3.86 2.97	
1287	Uninjured	Happy Valley, on Anderson ranch.	do	{ 12.10 8.01	.36 .27	2.97 3.37	X
1288	Injured			{ 8.01 9.53	.27 .32	3.37 3.35	
1289	Uninjured	Happy Valley, on Pickard ranch.	do	{ 9.53 8.17	.32 .20	3.35 2.45	Y
1290	Injured						

^a On outer edge of area acknowledged by company to be injured; all other samples were taken beyond this area.

NOTE.—By uninjured trees are meant those that show no discoloration or drying of leaves; they may, however, be somewhat stunted. By injured trees are meant those that show some discoloration, drying of leaves, and other unhealthy symptoms.

A glance at Table 4 shows that of the 25 groups of trees examined 20 groups, or 80 per cent, contained more sulphur trioxid in the leaves of the injured trees than in the leaves of the uninjured, while only 5 groups (E, I, J, L, R), or 20 per cent, showed the reverse. It is further shown that 80 per cent of the injured trees contained a larger percentage of sulphur trioxid in the ash than the uninjured trees, while only 20 per cent (C, E, L, R, X) showed the reverse.

It will be noted in groups I and J that although the uninjured tree contains slightly more sulphur trioxid than the injured one, yet the percentage of sulphur trioxid in the ash in both cases is much lower in the uninjured tree than in the injured. It would appear from this that the injured trees in these groups were undoubtedly killed by sulphur dioxid, but that the whole ash content of the uninjured trees, and consequently their sulphur trioxid content, was so much greater than that of the injured trees that even when the latter absorbed sulphur trioxid not enough was taken up to increase its percentage in the foliage over that naturally contained in the uninjured tree. For groups C and X the opposite is true; so that although in these groups the sulphur trioxid content of the injured tree is greater than that of the uninjured, it would appear that they were not killed by sulphur dioxid fumes.

Such an increase of the sulphur trioxid content of the injured trees over that of the uninjured trees in so large a number of cases must have some significance. It means either (1) that the injured trees grew in soils containing more sulphur trioxid than the uninjured trees; (2) that the injured were of a more vigorous growth than the uninjured trees, or (3) that the former absorbed more sulphur dioxid from the air than the uninjured trees. The first can not be the true cause, because the different groups of trees (one injured and the other uninjured) were taken near each other from the same soil, which on the average would give approximately the same amount of sulphur trioxid in both trees. The second can not be the true cause, for if the injured trees had been more vigorous they would have been the ones to live under the same conditions. The third, then, must be the true cause for this increased sulphur trioxid content in the injured trees.

It might be asked why all of the injured trees did not show a higher sulphur trioxid figure than the uninjured ones. It must be remembered in this connection that trees sometimes die of natural causes, and that in taking a large number of samples it was impossible for the chemist to tell which trees died from natural causes and which from sulphur dioxid fumes. The whole investigation is not intended to show that all injured and dead trees were affected by sulphur dioxid, but to show whether or not the large majority were.

Again it might be asked why one tree should be killed by sulphur dioxid and one close by not killed. This might be caused by several



VIEW ABOUT 2 MILES SOUTH OF SMELTER.





COUNTRY ABOUT 21 MILES SOUTH OF SMELTER.



circumstances. The air currents or the contour of the land might be such as to cause one tree to get more sulphur dioxid than the other, or one tree might be less vigorous and therefore more susceptible to the action of the sulphur dioxid than the other. For example, two men, one strong and the other weak, might be working side by side in some factory where they were both exposed to the same arsenic fumes. It is perfectly possible that the strong man might breathe the arsenic fumes day after day and not be affected, because of his superior excreting power, etc., while the weak man might die from the arsenic collected in his system on account of his inability to throw it off. If the bodies of both men could be examined more arsenic would undoubtedly be found in that of the dead man. The same conditions could easily exist in the case of trees.

ANALYSES OF FOLIAGE ABOUT A ZINC SMELTER AT LETMATHE, GERMANY.

In Haselhoff and Lindau's work on the Injury to Vegetation by Smoke and Fumes a large number of investigations upon this subject that have been made in Germany are collected. One of these on the injury to vegetation caused by the fumes of a zinc smelter at Letmathe is such an excellent example that a few of the tables will be given. In Table 5 are given the results obtained by making analyses of the leaves of trees situated in a westerly and southerly direction from the smelter, all expressed on a dry sand-free basis. Instead of selecting the trees in groups where some are injured and some not, the injured trees are in this table taken from near the smelter, and the uninjured ones from a greater distance but in the same direction.

TABLE 5.—*Sulphur trioxid content of foliage from trees about a zinc smelter at Letmathe, Germany.*

Description.	Ash in leaves or needles.	Sulphur trioxid.	
		In ash of leaves or needles.	In leaves or needles.
Pitch pine:	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Injured	5.56	11.78	0.656
Do.....	7.83	13.60	1.067
Uninjured	4.55	11.23	.512
Larch:			
Injured	5.50	22.84	1.258
Do.....	5.67	18.13	1.057
Do.....	6.32	21.55	1.364
Uninjured	4.93	21.54	1.063
Pine (Weymouth's kiefer):			
Injured	3.47	16.06	.559
Uninjured	3.38	14.91	.504
Pine:			
Injured	3.38	12.15	.411
Uninjured	3.99	2.75	.110
Oak:			
Injured	5.37	13.45	.723
Uninjured	4.62	12.29	.558
Beech:			
Injured	4.90	11.26	.552
Uninjured	3.93	11.51	.453

Of the nine different groups examined above it will be noted that in only one case, the larch, is the amount of sulphur trioxid in the injured tree less than that in the uninjured, and in only two cases is the amount of sulphur trioxid in the ash lower in the injured tree than in the uninjured. This is a somewhat better result than that obtained in the investigation made in California; but it must be remembered that the German forests are kept in a much better condition than our own, dead trees being removed, etc., so that these investigators did not stand so great a chance as the author of taking samples from trees which had died from natural causes.

In the following table are given the results obtained on examining the trees around the smelter some three or four years later:

TABLE 6.—*Result of second examination made at Letmathe about three years after the one recorded in Table 5.*

Description.	Distance from factory.	Direction from factory.	Sulphur trioxid in leaves or needles.
	<i>Minutes.</i>		<i>Per cent.</i>
Plum tree:			
Injured	25	Southwest	0.606
Uninjured	60	do517
Apple tree:			
Injured	5-20	do549
Do	25	do542
Uninjured	60	do441
Oak tree:			
Injured	15-20	do581
Uninjured	45	do498
Plum tree:			
Injured	20	West673
Do	45	do632
Uninjured	90	do589
Apple tree:			
Injured	45	do505
Uninjured	90	do359
Oak tree:			
Injured	25	do826
Uninjured	90	do492
Injured	45	do560
Pine tree:			
Injured	25	do696
Do	45	do546
Uninjured	75	do389
Plum tree:			
Injured	20	do661
Uninjured	90	do589
Apple tree:			
Injured	20	do547
Uninjured	90	do359
Cherry tree:			
Injured	20	do641
Uninjured	90	do555
Scotch fir tree:			
Injured	15	Northwest524
Uninjured	40	do481
Pine tree:			
Injured	15	do631
Uninjured	40	do444
Larch:			
Injured	15	do621
Uninjured	40	do548
Apple tree:			
Injured	20	do464
Do	20	do535
Uninjured	45	do373

It will be observed that in all groups examined in the above table the percentage of sulphur trioxid in the leaves is higher in the injured than in the uninjured plants, and that the sulphur trioxid content varies inversely with the distance from the smelter, i. e., the farther away from the smelter the less sulphur trioxid in the leaves. It is regretted that the distance from the smelter could not be considered more carefully in the California investigation, but, unfortunately, on account of the very wild nature of the country—the presence of high mountains, deep chasms, etc.—it was not possible to follow the course of the fumes far in any one direction. Even if it had been possible it is doubtful whether definite results could have been obtained, since the smoke really had no one definite path, but by reason of the mountainous nature of the country and the very narrow gorges the fumes followed a large and variable number of channels. Again the fumes would often drift over a high ledge and remain far above the ground, not touching even the tops of the trees for a considerable distance, so that any figures obtained on this basis would doubtless have been misleading.

COMPARISON AND DISCUSSION OF RESULTS.

In Table 7 the results obtained by the author upon pine trees are gathered together and compared with the results obtained upon eastern pines which had not been subjected to smelter fumes. It will be observed that practically all of the pines, both injured and uninjured, around the smelting works (which we will call the western pines) contain more sulphur trioxid than the eastern pines and that the average for the injured western pines is more than twice the average of the eastern, while the average for even the uninjured western pines is nearly twice as much as the average for the eastern. The percentage of sulphur trioxid in the ash is also much larger in the western than in the eastern pines. This must be due to one of two causes: Either the western pines absorbed more sulphur trioxid from the soil than the eastern pines or they absorbed more sulphur dioxid from the air. Analyses of both the eastern and western soils upon which these various trees grew show that the western soil does not contain any more sulphur trioxid than the eastern soils and therefore this increased sulphur trioxid content in the western trees is almost certainly due to an absorption of sulphur dioxid from the air. As stated above, this absorption might kill some trees and not kill others, but there is little doubt that if this absorption takes place year after year practically all of the trees in this region will be finally killed.

TABLE 7.—*Comparison of the sulphur trioxid content of eastern and western pines and of their soils.*EASTERN PINES (UNITED STATES DEPARTMENT OF AGRICULTURE GROUNDS)
NOT EXPOSED TO SMELTER FUMES.

Serial No.	Description of samples.	Ash in needles.	Sulphur trioxid.		Designation of group.
			In leaves and soil.	In ash.	
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
1310	Needles from longleaf pine in good condition	2.85	0.29	10.00	-----
1311	Needles from pine in good condition	3.88	.57	14.94	-----
1312	Needles from sugar pine in good condition	3.20	.41	12.81	-----
1313	Needles from pine in good condition	4.07	.37	9.09	-----
1314	Soil beneath this group of trees041		-----
	Average for eastern pines41	11.71	-----

WESTERN PINES FROM COUNTRY SURROUNDING SMELTER, REDDING, CAL.

	Pine needles:				
1236	Dead tree	5.71	0.84	14.71	} A
1237	Uninjured tree	4.37	.58	13.27	
1242	Dead tree	5.03	1.59	31.61	} B
1241	Uninjured tree	3.95	.87	22.02	
1249	Injured tree	5.01	.64	12.77	} E
1250	Uninjured tree	5.35	.74	13.83	
1301	Soil beneath Nos. 1249-1250039		
	Pine needles:				
1253	Dead tree	4.90	.87	17.75	} F
1254	Uninjured tree	4.66	.81	17.38	
1258	Dead tree	3.07	.55	17.91	} I
1260	Uninjured tree	4.94	.57	11.54	
1259	Injured tree	2.53	.56	22.13	} J
1260	Uninjured tree	4.94	.57	11.54	
1261	Injured tree	4.21	1.16	27.55	} K
1262	Uninjured tree	3.50	.68	19.43	
1263	Dead tree	3.25	.51	15.69	} L
1264	Uninjured tree	3.59	.89	24.79	
1268	Dead tree	5.30	.90	16.95	} N
1267	Uninjured tree	5.17	.74	14.31	
	Pine needles:				
1270	Dead tree	4.44	.71	16.00	} O
1271	Uninjured tree	4.36	.65	14.91	
1302	Soil beneath Nos. 1270 and 1271039		
	Pine needles:				
1272	Dead tree	5.71	1.02	17.86	} P
1274	Uninjured tree	4.44	.65	14.59	
1302	Soil beneath Nos. 1272 and 1274039		
	Pine needles:				
1273	Injured tree	5.79	1.25	21.59	} Q
1274	Uninjured tree	4.44	.65	14.59	
1302	Soil beneath Nos. 1273 and 1274039		
	Pine needles:				
1277	Injured tree	3.27	.66	20.19	} S
1278	Uninjured tree	2.84	.57	20.07	
1305	Soil beneath Nos. 1277 and 1278014		
	Pine needles:				
1283	Injured tree	2.46	.89	36.18	} V
1284	Uninjured tree	3.24	.64	19.75	
1306	Soil beneath Nos. 1283 and 1284049		
	Average for dead or injured trees87	20.64	
	Average for uninjured trees70	17.16	

In Table 8 the same figures are given as in Table 4, but they have been arranged in groups, according to the direction from the smelter, i. e., all trees in a northerly direction are in one group, all trees in a southerly direction in one group, etc. It will be noted that north of the smelter, in 100 per cent or all of the groups examined the injured trees contain more sulphur trioxid, both in the dried leaves and in the ash, than the uninjured trees. South of the smelter, in 86 per cent of the groups examined the injured trees contain more sulphur trioxid than the uninjured, and in 71 per cent of the groups exam-

ined the ash of the injured trees contains a larger percentage of sulphur trioxid than the ash of the uninjured trees. East of the smelter, in 75 per cent of the cases examined the injured trees contain more sulphur trioxid than the uninjured trees, both in the dried leaves and in the ash, and west of the smelter, in 67 per cent of the groups examined the injured trees contain more sulphur trioxid than the uninjured ones, while in 78 per cent of the groups examined the sulphur trioxid content of the ash of the injured trees is higher than that of the uninjured trees. It would be expected that more trees in a northerly and southerly direction would be killed by the sulphur dioxid fumes than in an easterly or westerly direction because of the prevailing winds, and this expectation is justified by the above figures.

TABLE 8.—*Study of sulphur trioxid content of foliage of trees in California, arranged according to direction from smelter.*

TREES NORTH OF SMELTER.

Serial No.	Description of sample.	Approximate distance from smelter.	Ash in foliage.	Sulphur trioxid.		Designation of group.
				In foliage.	In ash.	
	Pine needles:		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
1236	Dead tree.....	3½ miles northwest	{ 5.71	0.84	14.71	A
1237	Uninjured tree.....		{ 4.37	.58	13.27	
1268	Dead tree.....	2 miles northeast	{ 5.30	.90	16.95	N
1267	Uninjured tree.....		{ 5.17	.74	14.31	
1270	Dead tree.....	3½ miles northeast	{ 4.44	.71	16.00	O
1271	Uninjured tree.....		{ 4.36	.65	14.91	
1272	Dead tree.....do	{ 5.71	1.02	17.86	P
1274	Uninjured tree.....do	{ 4.44	.65	14.59	
1273	Injured tree.....do	{ 5.79	1.25	21.59	Q
1274	Uninjured tree.....do	{ 4.44	.65	14.59	

TREES EAST OF SMELTER.

1275	Oak leaves:					
1276	Injured tree.....	1½ miles.....	{ 6.29	0.32	5.09	R
	Uninjured tree.....		{ 5.81	.40	6.89	
1277	Pine needles:					
1278	Injured tree.....do	{ 3.27	.66	20.19	S
	Uninjured tree.....		{ 2.84	.57	20.07	
1280	Oak leaves:					
1279	Injured tree.....	2½ miles.....	{ 7.88	.51	7.47	T
1281	Uninjured tree.....		{ 7.23	.41	5.67	
1279	Injured tree.....do	{ 5.90	.60	10.17	U
	Uninjured tree.....		{ 7.23	.41	5.67	

TREES SOUTH OF SMELTER (ALL LOCATIONS EAST OF SHASTA CALLED SOUTH).

1242	Pine needles:					
1241	Dead tree.....	2½ miles.....	{ 5.03	1.59	31.61	B
1241	Uninjured tree.....		{ 3.95	.87	22.02	
1263	Dead tree.....	3 miles.....	{ 3.25	.51	15.69	L
1264	Uninjured tree.....		{ 3.59	.89	24.79	
1265	Oak leaves:					
1266	Injured tree.....do	{ 8.88	.53	5.96	M
	Uninjured tree.....		{ 9.18	.25	2.72	
1283	Pine needles:					
1284	Injured tree.....	9 miles.....	{ 2.46	.89	36.18	V
	Uninjured tree.....		{ 3.24	.64	19.75	
1285	Peach leaves:					
1286	Injured tree.....do	{ 10.75	.45	4.19	W
	Uninjured tree.....		{ 8.29	.32	3.86	
1287	Peach leaves:					
1288	Injured tree.....	9 miles.....	{ 12.10	.36	2.97	X
1288	Uninjured tree.....		{ 8.01	.27	3.37	
1289	Injured tree.....do	{ 9.53	.32	3.35	Y
1290	Uninjured tree.....		{ 8.17	.20	2.45	

TABLE 8.—*Study of sulphur trioxid content of foliage of trees, etc.—Continued.*

TREES WEST OF SMELTER.

Serial No.	Description of sample.	Approximate distance from smelter.	Ash in foliage.	Sulphur trioxid.		Designation of group.
				In foliage.	In ash.	
	Bean leaves:		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
1243	Injured vine.....	} 2½ miles.....	{ 25.03	1.06	4.23	} C
1245	Uninjured vine.....		{ 18.87	.98	5.19	
	Peach leaves:					
1248	Injured tree.....	} do.....	{ 15.75	.72	4.57	} D
1247	Uninjured tree.....		{ 13.13	.51	3.88	
	Pine needles:					
1249	Injured tree.....	} 3¼ miles.....	{ 5.01	.64	12.77	} E
1250	Uninjured tree.....		{ 5.35	.74	13.83	
1253	Dead tree.....	} 5 miles.....	{ 4.90	.87	17.75	} F
1254	Uninjured tree.....		{ 4.66	.81	17.38	
	Blackberry leaves:					
1255	Vine nearly dead....	} do.....	{ 5.52	.47	8.52	} G
1256	Uninjured vine.....		{ 6.38	.27	4.08	
1257	Injured vine.....	} do.....	{ 7.11	.59	8.30	} H
1256	Uninjured vine.....		{ 6.38	.27	4.08	
	Pine needles:					
1258	Dead tree.....	} do.....	{ 3.07	.55	17.91	} I
1260	Uninjured tree.....		{ 4.94	.57	11.54	
1259	Injured tree.....	} do.....	{ 2.53	.56	22.13	} J
1260	Uninjured tree.....		{ 4.94	.57	11.54	
1261	Injured tree.....	} 6 miles.....	{ 4.21	1.16	27.55	} K
1262	Uninjured tree.....		{ 3.50	.68	19.43	

In connection with this study it might be of value to give some idea of the amount of sulphur dioxid that is given off each day into the atmosphere by the smelter. Analyses of three samples of the ore show that it contains 41.87, 40.06, and 42.44 per cent sulphur, or 41.46 per cent sulphur on the average. Since in extracting the copper the sulphur is nearly all given off as sulphur dioxid, it seems safe to assume that 90 per cent of the sulphur from this ore would be liberated. Therefore a simple calculation will show that for each ton of ore about 838 pounds of sulphur or 1,676 pounds of sulphur dioxid would be given off into the atmosphere. The author has been informed that this plant extracts 1,000 tons of ore per day. If such is the case, it will be seen that the enormous quantity of 1,676,000 pounds of sulphur dioxid (or 748 tons) are given off each day.

An analysis of the water from a creek which runs alongside the smelter and empties into the Sacramento River was made, and it was found that the water was not only very acid, but contained a trace of arsenic and 1 milligram of dissolved copper per liter. It can easily be seen that these constituents might have an extremely injurious action upon fish, upon crops irrigated by the Sacramento, and upon persons who might drink the water.

GENERAL CONCLUSIONS.

The following conclusions may be drawn from this investigation:

1. Sulphur dioxid when present in very small quantities in the air kills vegetation.
2. Such injury shows itself by the increased sulphur trioxid content of the foliage.

3. The vegetation around the smelter for at least $3\frac{1}{2}$ miles north, 9 miles south, $2\frac{1}{2}$ miles east, and 5 to 6 miles west has been greatly injured.

4. The water of the Sacramento River is polluted by the waste material from the smelter.

5. It is the opinion of the author that this injury to vegetation will continue and even increase its limits unless the fumes are condensed.

6. The fumes can be condensed and sulphuric acid formed, for which a ready market would probably be found.

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